Roughness and wettability of aligner materials

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Abstract: OBJECTIVE: The characterisation of surface roughness and energy of contemporary thermoplastic materials used in manufacturing of orthodontic aligners. DESIGN: In vitro, laboratory study. MATERIALS AND METHODS: Four commercially available thermoplastic materials were selected (CA-medium/CAM, Essix-copopyester/COP, Duran/DUR and Erkodur/ERK). Five disks from each, as received, material were tested and subjected to: (1) reflected light microscopy; (2) optical profilometry for the estimation of Sa, Sz, Sq, Sdr, Sc, Sv surface roughness parameters (n = 5); and (3) contact angle measurements with a Zisman series of liquids for the estimation of critical surface tension ($_C$), total work of adhesion (W^A), as well as the work of adhesion due to polar (W^P) and dispersion (W^D) components employing the Zisman method (n = 5/liquid). Thermoformed disks were prepared against a dental stone model and the roughness parameters were calculated again Statistical analysis was performed by one-way ANOVA/ Tukey multiple comparison test and t-test (a = 0.05). RESULTS: Microscopic and profilometric analyses revealed a smooth surface texture in the as-received materials, but a very rough texture after thermoforming, with insignificant differences within each state. Significant differences in the as-received state were found in the surface energy parameters; CAM showed the lowest $_C$ and the highest W^A, W^P, W^D, whereas ERK with the highest $_C$ demonstrated lower W^A. COP and DUR were ranked in an intermediate group regarding $_C$, with a statistically significant difference in W^A between them, mainly attributed to the lower W^P of the former. CONCLUSION: Given the differences in surface energy parameters and the lack of roughness differences within the as received or thermoformed groups, it may be concluded that variations in the plaque retaining capacity are anticipated, determined by $_C$, W^A and the W^P, W^D components.

DOI: https://doi.org/10.1177/1465312520936702

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J Orthod 2020;47:223-31

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ABSTRACT

Objective: The characterization of surface roughness and energy of contemporary thermoplastic materials used in manufacturing of orthodontic aligners.

Design: In vitro, laboratory study.

Materials and Methods: Four commercially available thermoplastic materials were selected (CA-medium/CAM, Essix-copopyester/COP, Duran/DUR and Erkodur/ERK). Five disks from each, as received, material were tested and subjected to a) reflected light microscopy, b) optical profilometry for the estimation of Sa, Sz, Sq, Sdr, Sc, Sv surface roughness parameters (n=5) and c) contact angle measurements with a Zisman series of liquids for the estimation of critical surface tension (γ_C), total work of adhesion (W^A), as well as the work of adhesion due to polar (W^P) and dispersion (W^D) components employing the Zisman method (n=5/liquid). Thermoformed disks were prepared against a dental stone model and the roughness parameters were calculated again Statistical analysis was performed by one-way ANOVA/ Tukey multiple comparison test and t-test (a=0.05).

Results: Microscopic and profilometric analyses revealed a smooth surface texture in the as received materials, but a very rough texture after thermoforming, with insignificant differences within each state. Significant differences in the as-received state were found in the surface energy parameters; CAM showed the lowest γ_C and the highest W^A, W^P, W^D, whereas ERK with the highest γ_C demonstrated lower W^A. COP and DUR were ranked in an intermediate group regarding γ_C, with a statistically significant difference in W^A between them, mainly attributed to the lower W^P of the former.

Conclusions: Given the differences in surface energy parameters and the lack of roughness differences within the as received or thermoformed groups, it may be concluded that variations in the plaque retaining capacity are anticipated, determined by γ_C , W^A and the W^P, W^D, components.

KEYWORDS orthodontic aligners, 3D-roughness, surface energy, wettability, plaque retention

Introduction

Numerous studies have shown that fixed orthodontic appliances are associated with higher risk of enamel white spot formation, caries and gingivitis during treatment (Ireland et al., 2014; Mizrahi, 1983; Gorelick et al., 1982; Heymann and Grauer, 2013; Bollen et al., 2008). The changes induced in the oral environment, such as the increased surface area provided for bioadhesion, microbial colonization and pH reduction at the vicinity, have been found to promote the development of enamel decalcification during active orthodontic treatment (Balenseifen and Madonia, 1970; Rosenbloom and Tinanoff, 1991; Menzaghi et al., 1991). Concurrently, the demand of patients for aesthetic orthodontic treatment has been increased with clear aligners becoming increasingly popular (Rosvall et al., 2009), since the amount of clinical reports on the risks associated with removable appliances is still low compared with the available for fixed appliances.

It has been documented that aligners retain less plaque and have lower incidence of gingival inflammatory reactions compared to fixed appliances (Abbate et al., 2015; Jiang et al., 2018). Nevertheless, it has been postulated that significantly supragingival microbiological changes occur in the presence of fixed and removable appliances (Petti et al., 1997). The issue of bioadhesion and the resultant pellicle and plaque formation are mainly dependent on surface morphology, surface chemistry and surface charge, with the latter having negligible influence under physiologic ionic conditions (Baier, 1988). Hence, the changes in the oral environment depend not only on the design of the appliance, but also on the material structure and properties (Ireland et al., 2014; Forsberg et al., 1991), which dominate bacteria adhesion (Ahn et al., 2006; Ahn et al., 2007; Lim et al., 2008). A typical example is the significantly higher adhesion of cariogenic streptococci than on bracket materials (Lim et al., 2008).

Intraoral bacterial adhesion to surfaces proceeds in four stages: a) Bacteria transportation to the surface via Brownian motion or chemotactic activity, b) initial adhesion, controlled by long-range interaction forces, c) attachment mediated by primary/secondary bonding, direct contact or extracellular filament bridging, and d) microbial colonization (Quirynen, 1994; Gibbons, 1989). Within this process, surface roughness and surface free energy of the substrate have been found to play a key role, with the former having a more important influence (Quirynen, 1994). An increased surface roughness accelerates pellicle adsorption, plaque formation and maturation by providing increased surface area for bacteria retention and stagnation zones of minimal dislodging shear forces that stabilize bacteria adsorption during their initial reversible binding phase. An energetically reactive substrate possessing high surface free energy, enhances formation of oral integuments from microbial strains of high surface free energy and vice versa. Since both these parameters are simultaneously implicated in microbial attachment phenomena, smooth surfaces with low surface tension are preferred to avoid plaque accumulation (Quirynen and Bollen, 1995). The role of critical surface tension on the early retention of microorganisms from unstimulated human saliva has been investigated in detail by Christensen et al (1989). The authors concluded that morphotype retention is non-specific, as it is strongly dependent on the mechanical removal forces and the surface energy of the substrate.

Despite the fact that the plaque-retaining capacity of different bracket materials, resin composite cements, dental implants and biomaterials has been investigated (Eliades et al., 1995; Glauser et al., 2017; Wassmann et al., 2017), limited information exists on the surface roughness and energy of thermoplastic materials used in manufacturing orthodontic clear aligners. Although these

appliances are not used intraorally for more than two weeks, there is evidence of biofilm formation and calcification on their internal surfaces adjacent the teeth (Papadopoulou et al., 2019).

The purpose of this study was the characterization of the surface roughness and energy of contemporary thermoplastic materials used in manufacturing of orthodontic aligners, which greatly modulate their plaque-retention capacity. The null hypothesis was that no significant differences exist among the materials tested in surface roughness and energy.

Materials & Methods

Materials

Four commercially available thermoplastic materials used for aligner manufacturing were selected for the study. The brand names, composition, manufacturers and codes of the materials used are presented in Table 1. The surface roughness and texture of raw materials was assessed by reflected light microscopy and optical profilometry a) as received, and b) after thermoforming on flat hard dental stone surfaces polished with SiC papers up to 1200 grit-size. The surface energy of the row materials was determined by contact angle measurements with a Zisman series of liquids.

Reflected light microscopy

Five disks from each material were inspected under an optical microscope (DM 4000B, Leica, Wetzlar, Germany) operated in reflection mode under bright-field and a 100X magnification.

Optical Profilometry

Five disks from each material were tested with an optical interferometric profiler (Wyko NT1100, Veeco, Tunscon, AZ, USA). Measurements were taken from the center of each disk (n=5) under the following conditions: Mirau lens, at 40× magnification (113.3×148.5 μm^2 analysis area), vertical scanning mode, 2% modulation and tilt correction. The surface roughness parameters recorded were: a) The amplitude parameter Sa (the arithmetic mean of the absolute values of the surface height deviations measured from the best fitting plane), b) the amplitude parameter Sz (the ten-point height over the surface, representing the average difference between the five highest peaks and five lowest valleys), c) the amplitude parameter Sq (root mean square roughness), d) the hybrid parameter Sdr (the developed area due to the surface texture versus an ideal plane area ratio), e) the functional parameter Sc (core void volume, the volume supported by the surface from 10% to 80% of the bearing ratio) and f) Sv (surface void volume, the volume the surface would support from 80% to 100% of the bearing ratio).

Contact Angle Measurements

The contact angles (θ) of a Zisman series of liquids with the intact specimen surfaces were investigated according to the sessile drop methodology (Glantz, 1969). The liquids used along with their liquid-vapor surface tension (γ_{LV}) and their corresponding polar (γ^P_{LV}) and non-polar or dispersion (γ^D_{LV}) components are presented in Table 2. For contact angle measurements a custom made system was used based on the principles described by Lamour et al (2010). Each specimen was transferred on a horizontally leveled microadjustable reading table and a 10 μL drop of each liquid was applied from a 5 mm height employing a microsyringe (Hamilton, Reno, NV, USA). A cylindrical cup of transparent glass (50 mm diameter, 80 mm height) was used to cover the sessile drop and a hallow plate (20 mm

diameter, 2 mm height) filled with the same liquid to provide a saturated atmosphere. Droplet spreading patterns were illuminated by a LED fiber optic with a diffuser and photographed utilizing a digital camera equipped with a 105 mm lens. All experiments were carried out under the same environmental conditions (T=23^{o}C, RH: 50%). The contact angle (θ) developed between the plane surface and the liquid drop was photographed 10 s after application and the angle was calculated trigonometrically from the height (h) and base (b) dimensions of the meniscus formed (θ = 2 arctan 2h/b). Five measurements were taken on each disk. The cosine of the contact angle θ (cosθ) in combination with the liquid-vapor surface tension values of each liquid (γ_{LV}) were used to calculate the total work of adhesion W^A, as well as the work of adhesion due to polar W^P and non-polar or dispersion W^D forces (Glantz, 1969; Eliades et al., 1995). The data of liquid vapor surface tension (γ_{LV}) along with the corresponding cosθ values were linearly fitted and the intersection of each line with cosθ=1 was used to determine the critical surface tension (γ_C).

Statistical analysis

All data were tested for normality by Kolmogorov-Smirnov and homoscedasticity by equal variance tests. The results of γc, W^A, W^P, W^D were subjected to one-way analysis of variance (ANOVA) and Tukey multiple comparison post hoc test, employing the material as discriminating factor. For comparison of the roughness parameters between as received and thermoformed states, a two-way ANOVA was selected (material and status discriminating factors). However since an interaction was found the data were broken down and the effect of the status was evaluated per material by t-tests. In all cases the level of significance was set at a=0.05. The statistical analysis was performed by SigmaStat software (SigmaPlot v.12.5, Systat Software Inc, San Jose, CA, USA).

Results

Reflected-light microscopic images of the material surfaces are illustrated in Fig. 1. The as received materials demonstrated a smooth surface texture with some scratches possibly assigned to the production process (Fig. 1 A, B). Thermoformed materials demonstrated distinctive features associated with their malleability under high temperature, such as shear thinning zones (Fig. 1 C) and unidirectional striations (Fig. 1D).

Representative 3D-profilometric images of the material surfaces after thermoforming are given in Figure 2. In the as received state, the materials demonstrated a very smooth topography, which was modified to a more irregular one after thermoforming. Parallel striations were apparent in all materials after thermoforming, with the greatest inter-striation distance observed in DUR. Onto this structure peaks of various densities were observed, with the most prominent detected in ERK. The results of the roughness parameters are summarized in Table 3. There was no statistically significant difference among the materials in the as received or thermoformed states with the mean parameter values ranging within 8.1-9.6 nm (Sa), 54.8-96.3 nm (Sz), 11.2-13.4 nm (Sq), 0-0.002 % (Sdr), 12-14.3 nm^3/nm^2 (Sc) , 1-1.3 nm^3/nm^2 (Sv) for the former and 80.8-100.3 (Sa), 1023-1153 nm (Sz), 112.6-138.7 nm (Sq), 0.84-1.23 % (Sdr), 134-172.2 nm^3/nm^2 (Sc), 4.8-8.2 nm^3/nm^2 (Sv) for the latter. Nevertheless, a statistically significant difference was registered for all the parameters before and after thermoforming.

Figure 3 illustrates representative images of the contact angles of testing liquids on as received material surfaces, from where the surface energy parameters were calculated. The contact angles were progressively decreased from the most (water) towards the least polar liquid (1-bromonaphtalene).

The Zisman plots used for calculation of the critical surface tension are illustrated in Fig. 4. The results of the surface energy parameters tested are illustrated in Table 3. The ranking of the statistically significant differences were: ERK>CAM with insignificant differences of COP and DUR from both for γ_C; CAM>DUR,ERK>CAM, for W^A; CAM>ERK>COP with insignificant differences of DUR from CAM and ERK, for W^P and CAM>COP,DUR with insignificant differences of ERK from all for W^D. The polar fraction of the W^A (W^P) was slightly greater in CAM, DUR and lower in ERK than the W^D within a 0.7-1.4 erg/cm^2 difference range in absolute values. Nevertheless, COP demonstrated a much higher difference (6.7 erg/cm^2) in favor of the dispersive component.

DISCUSSION

Based on the experimental results of this study the null hypothesis was not rejected only for surface roughness, since significant differences were encountered in surface energy.

In the present study, raw materials were used for determination of the surface energy, instead of end products. The main reasons were a) to avoid changes in the surface chemistry due to contamination during thermoforming from the stone material, and b) to exclude the changes in specimen roughness induced by the thermoforming procedure, as documented in the present study, which influence the surface energy measurements (Glanz, 1969). Although testing raw materials may not represent the clinical scenario, measuring contact angles on an aligner with full 3D-geometrical fidelity (presence of curved regions, pitts, fissures, etc) is unreliable and may affect the droplet shape upon the spreading equilibrium period. Under these conditions, the reference materials may provide the ultimate performance regarding surface energy and roughness.

The materials used were mainly composed of polyethylene glycol terephthalate-PETG (Gardner et al., 2003; Ryokawa et al., 2006; Pascual et al., 2010; Alexandropoulos et al., 2015). No polyurethane-based materials were tested, such as Invisalign (Alexandropoulos et al., 2015; Gracco et al., 2009), since the raw material of this product is not available. All reference samples demonstrated similar surface morphology with a smooth texture and few scratches, which should be appended to surface finishing during the manufacturing process. The reference samples showed very low Sa values (< 20 nm). As surface roughness strongly interferes with wetting phenomena (Glantz, 1969), the very low Sa values registered validate the direct comparison of the surface energy properties among the materials tested.

In the present study the critical surface tension (γ_C) and the concept of polar and dispersion components of γ and W^A, than the Lewis acid-base interfacial interactions approach (Good and van Oss, 1991) was used to calculate surface free energy parameters. The main reason was that the latter is more suitable for polar surfaces such as inorganic, organometallic and ionic (Spooner, 2018), and several times unexplained negative square roots appear, leading to a number of objections to the theory (Erbilm, 2010). The γ_C of a solid surface, expresses the highest surface tension value of a liquid needed to completely wet a solid. The lower γ_C of CAM denotes that it is less prone to liquid wetting in comparison with ERK. Previous studies have reported that human saliva has surface tension values within the range of 53 to 60 dyn/cm (Glantz, 1969), although these can be strongly affected by experimental and methodological parameters (Baier et al., 1984). Under these limitations, it may be concluded that all the PETG aligners tested are partially wetted by human saliva, with CAM demonstrating the least wettability.

The total work of adhesion (W^A), provides an insight into the retention capacity of the intraoral biofilm developed, since a higher W^A is associated with higher retention. Therefore, it may be postulated that differences in W^A have a clinical impact within the context of pellicle formation. The tested materials showed differences in W^A; CAM demonstrated the highest values, followed by COP and the statistically homogeneous group of DUR and ERK. All the materials showed values much higher than the range of 30-50 erg/cm^2 which has been suggested as the induction threshold for biological adhesion (Jendresen and Glantz, 1981). The performance of CAM has some interesting characteristics since it is classified in the lowest group of γ_C, and the highest of W^A, W^P and W^D; these imply that although CAM is less prone to wetting, the retentive capacity of the adsorbed fractions is quite strong. On the other hand ERK with the highest wettability, as expressed by γ_C, demonstrated significantly lower W^A from CAM and hence a more easily removal of the adsorbed fractions. Consequently, a single property like γ_C may not precisely express the mechanisms involved in the adsorption and desorption processes of intraoral integuments. COP and DUR were ranked in an intermediate statistically homogeneous group regarding γ_C, with a statistically significant difference in W^A between them, mainly attributed to the lower W^P of the former. This suggests that hydrophobic interactions are of particular importance in COP.

All the materials tested were glycol-modified polyethylene terephthalate (PETG) co-polymers. PETG is a non-crystallizing transparent amorphous copolymer, with no strain-induced crystallization. It is usually composed of 31% mol of poly (1,4-cyclohexylenedimethylene terepthalate/PCT) and 69 mol% of polyethylene terepthalate/PET). Upon deformation PETG develops a rigid amorphous phase which contrary to PET does not crystallize. Both the materials demonstrate a stiffer response in plain strain compression than in uniaxial compression, with the strain hardening being much less in PETG (Dupaix

and Boyce, 2005). The different surface chemistry of the PETG products associated with the fraction of PCT content in PETG, may explain these surface chemistry differences, since an increase in PCT has been associated with increased reactivity, and hydrophilic nature (Chen et al, 2016).

Roughness has long been shown to affect contact angle measurements since the early work of Wenzel (1936). Generally, increased roughness has a positive effect on wettability, decreasing the contact angle. Nevertheless, there is no linear correlation between roughness and contact angle. For several materials the water contact angle is very high at very low amplitude roughness values (0.1 μm), as registered by Ra measurements, then reduced at middle range values (1 μm) and increases again at higher values (10 μm) (Kubiak et al, 2011). These changes are mostly associated with the increase in the solid-liquid interface area of the rough surface in relation to the projected smooth surface.

The results of roughness after thermoforming were much higher than the reference materials, as expected, with the most affected being the amplitude parameter Sz and the functional parameter Sc. These changes should be appended to the roughness of the dental stone model against which the aligners were thermoformed and to the material properties associated with the shear thinning phenomena during the thermal treatment. The values recorded for the thermoformed PETG materials were much lower than the reported for a polyurethane aligner manufactured by stereolithography, milling and polishing (Papadopoulou et al., 2019). Prior work has documented the acceleration of plaque formation with an increase mainly in amplitude surface roughness (Quirynen and Bollen, 1995); However, a proper analysis of surface roughness requires approximately 14 parameters (Wennerberg and Albrektsson, 2000; Stout and Blunt, 2000). A standard set of topographical, bacterial adhesion-relevant roughness parameters, has been provided by Crawford et al.(2012). For this reason more parameters representing amplitude, hybrid and functional types were introduced in the present study.

The reported roughness parameters would be useful in establishing a context of results for the plaque retaining capacity of orthodontic material surfaces. The results of the study may be used to interpret the findings of a clinical investigation, which concluded that there were no significant differences between the oral microbiota changes in the saliva of patients treated with fixed appliances or thermoplastic aligners (Sifakakis et al., 2018).

Under the limitations of the present study it may be concluded that in the absence of statistically significant differences in the roughness parameters tested within the as received and the thermoformed groups, the differences registered in the surface energy parameters may control biofilm formation and plaque development on the aligners tested.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The authors received no financial support for the research, authorship, and/or publication of this article.

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TABLES

Table 1. The aligner materials used in the study.

Product	Code	Composition	Manufacturer
CA-medium	CAM	polyethylene glycol terephthalate (PETG)	Scheu-Dental, Iserlohn, Germany
Copolyester	COP	polyethylene glycol terephthalate (PETG)	Essix, Dentsply Raintree Essix, Sarasota, FL, USA
DURAN	DUR	polyethylene glycol terephthalate (PETG)	Great Lakes Dental Technologies, Tonawanda, NY, USA
ERKODUR	ERK	polyethylene glycol terephthalate (PETG)	Erkodent Erich Kopp, Pfalzgrafenweiler, Germany

Table 2. Liquid-vapor surface tension values (γ_{LV}) of the liquids used in this study with the corresponding polar (γ^{P}_{LV}) and non-polar (γ^{D}_{LV}) components (Glanz, 1969).

Liquid	γ_{LV} (dyn/cm)	γ^{P}_{LV} (dyn/cm)	γ^{D}_{LV} (dyn/cm)
Water	72.6	50.8	21.8
Glycerol	63.4	26.4	37.0
Thiodiglycol	54.0	15.5	38.5
Diiodomethane	50.8	-*	50.8
1-bromonapthalene	44.6	-*	44.6

* There is no polar component for these liquids

Table 3. Mean values and standard deviations (in parentheses) of the surface roughness parameters as received (a) and after thermoforming (b). Same superscript letters denote values without statistical significant differences per parameter within and between a, b treatment groups ($p>0.05$).

Group	Sa (nm)	Sz (nm)	Sq (nm)	Sdr (%)	Sc (nm^3/nm^2)	Sv (nm^3/nm^2)
a) As received						
CAM	8.1 (2.8)^{a}	54.8(22.6)^{a}	13.1 (7.5)^{a}	0.002 (0.004)^{a}	12.0 (3.8)^{a}	1.0 (0.3)^{a}
COP	8.5 (0.6)^{a}	58.0(3.5)^{a}	11.2 (1.2)^{a}	0.000 (0.000)^{a}	12.5 (0.9)^{a}	1.3 (0.2)^{a}
DUR	9.6 (2.5)^{a}	96.3(24.1)^{a}	13.4 (4.8)^{a}	0.000 (0.000)^{a}	14.4 (3.1)^{a}	1.1 (0.2)^{a}
ERK	9.0 (2.0)^{a}	75.7(26.4)^{a}	12.6 (3.2)^{a}	0.000 (0.000)^{a}	13.9 (3.2)^{a}	1.0 (0.2)^{a}
b) After thermoforming						
CAM	94.3 (5.8)^{b}	1090 (281)^{b}	128.2 (5.2)^{b}	1.12 (0.18)^{b}	169.5 (11.1)^{b}	7.4 (2.1)^{b}
COP	80.8 (13.4)^{b}	1023 (243)^{b}	112.6 (23.0)^{b}	1.23 (0.41)^{b}	134.0 (19.8)^{b}	7.2 (1.1)^{b}
DUR	85.5 (9.2)^{b}	1153 (147)^{b}	121.5 (8.8)^{b}	0.84 (0.11)^{b}	162.4 (25.5)^{b}	4.8 (0.2)^{b}
ERK	100.3 (8.0)^{b}	1130 (88)^{b}	138.7 (6.8)^{b}	1.11 (0.15)^{b}	172.2 (14.9)^{b}	8.2 (3.2)^{b}

Table 4. Mean values and standard deviations (in parentheses) of critical surface tension (γ_C), total work of adhesion W^A and work of adhesion due to polar (W^P) and dispersion (W^D) components and their differences (Δ) for all the materials tested in the as received state. Same superscripts denote mean values without statistical significant differences ($p>0.05$).

Group	γ_C (dyn/cm)	W^A (erg/cm^2)	W^P (erg/cm^2)	W^D (erg/cm^2)	$\Delta(W^P-W^D)$ (erg/cm^2)
CAM	40.3 (0.9)^{a}	96.3 (3.5)^{a}	48.5 (3.5)^{a}	47.8 (0.8)^{a}	0.7
COP	43.8 (3.0)^{a,b}	84.3 (4.6)^{b}	38.8 (4.4)^{b}	45.5 (2.0)^{b,c}	-6.7
DUR	43.2 (2.4)^{a,b}	92.0 (4.5)^{c}	46.7 (3.9)^{a,c}	45.3 (2.1)^{b,c}	1.4
ERK	45.6 (0.6)^{b}	90.3 (2.9)^{c}	44.5 (2.8)^{c}	45.8 (2.9)^{a,c}	-1.3

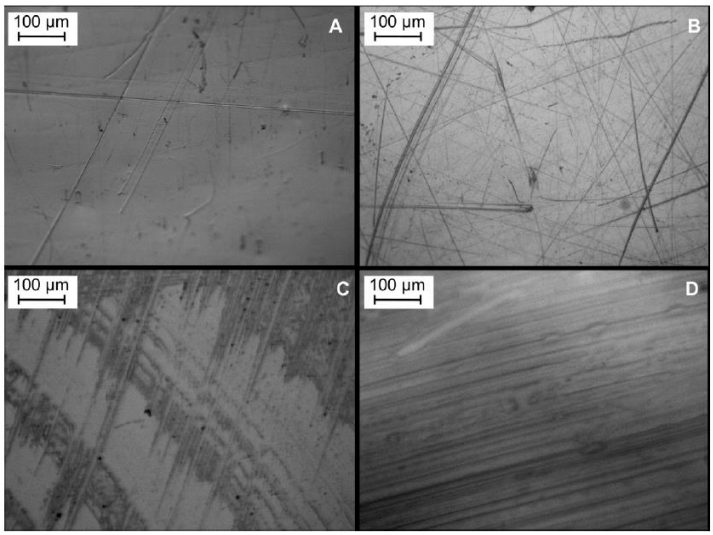
LEGENDS OF FIGURES

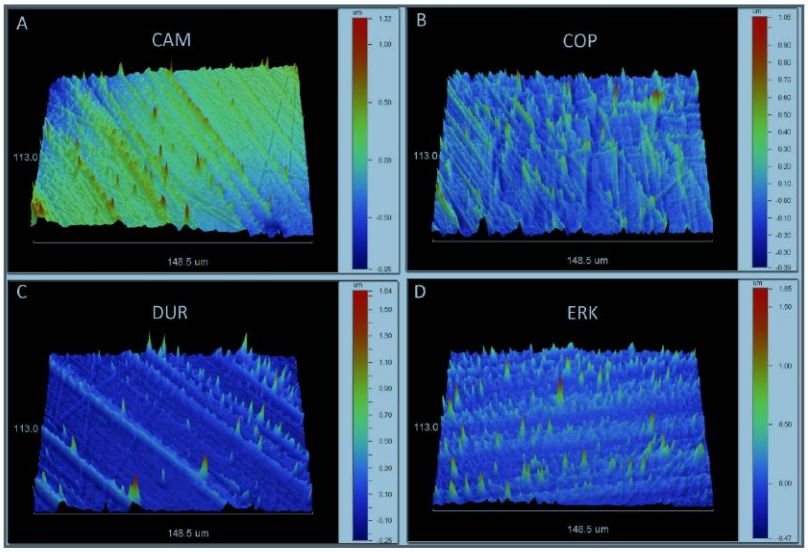
Figure 1. Reflected light images of as received (A: CLA, B: ERK) and thermoformed (C: COP, D: DUR) aligner materials. The striations assigned to shear thinning after thermoforming are apparent in C and D (100× magnification, bar = 100 µm).

Figure 2. Representative 3D optical profilometric images of the thermoformed materials tested. Note the differences in amplitude scales (A: CAM, amplitude scale -0.95 to 1.22 µm; B: COP, amplitude scale -0.39 to 1.06; C: DUR, amplitude scale -0.25 to 1.64; D: ERK, amplitude scale -0.47 to 1.65 µm, 40× magnification).

Figure 3. Contact angle images of the Zisman liquids on DUR: A) water, B) glycerol, C) thiodiglycol, D) diiodomethane and E) 1-bromonapthalene.

Figure 4. Zisman plots for calculation of the critical surface tension (γ_C) of the materials tested by linear fitting the experimental data.





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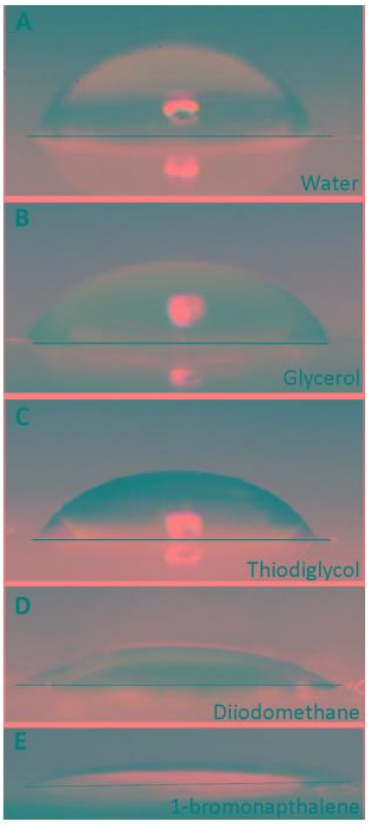

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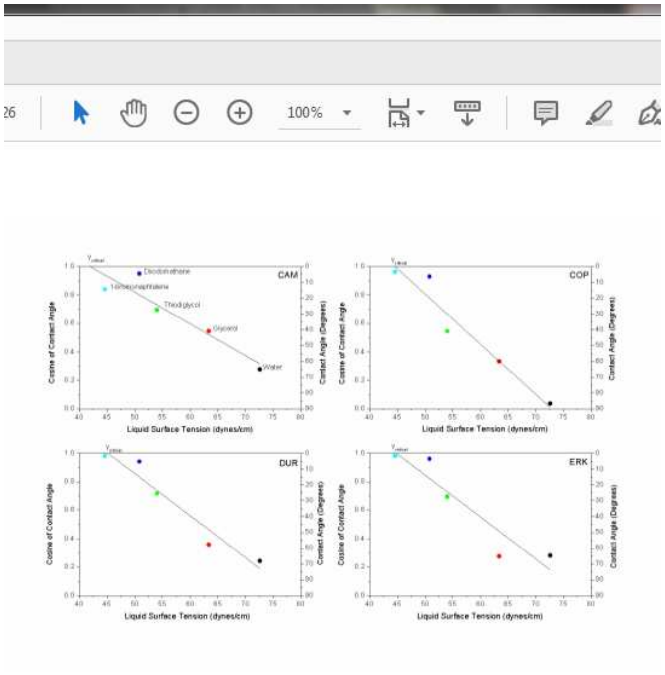

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